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# Photovoltaic solar electrodialysis with bipolar membranes

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ABSTRACT

Electrochemical process like Electrodialysis (ED) and Electrodialysis with Bipolar Membranes (EDBM) can contribute to the production of freshwater and to the valorization of waste streams. In particular, EDBM can valorise the waste from desalination technologies using electric power, producing acids (HCl) and basis (NaOH) from seawater rejected brines. The use of a variable current intensity coming from a low-carbon source such as photovoltaic (PV) solar energy means a decrease of the associated carbon footprint of the obtained products. In this work, the reduction of the specific energy consumption (SEC) of the acid from an EDBM process thanks to a feedback control loop under variable current intensity is presented. The EDBM process works in continuous or semi-continuous mode under constant or variable current intensity by means of a PV solar array simulator for 30 h. A concentration around 1 mol·L$^{-1}$ HCl has been obtained in all experiments even under variable current intensity. A noticeable drop in the SEC from a reference value of 7.3 kWh·kg$^{-1}$ HCl (constant current intensity) to 4.4 kWh·kg$^{-1}$ HCl (variable current intensity and feedback control loop) was reported.

## 1. Introduction

Electrochemical process like Electrodialysis (ED) and Electrodialysis with Bipolar Membranes (EDBM) can contribute to the production of freshwater and to the valorization of waste streams. In particular, EDBM is capable of producing acids such as HCl and bases such as NaOH from the waste of the desalination technologies in the form of brines using electricity as a driver. Indeed, the most critical limitation of using EDBM for acid and basis production is related to this energy consumption, which also affects the operation costs [1]. An example of reported values for the Specific Energy Consumption (SEC) of EDBM is between 7.5 kWh·kg$^{-1}$ HCl and 8.3 kWh·kg$^{-1}$ HCl [2]. Therefore, the generation of the demanded electrical energy for the EDBM will have a certain carbon footprint, depending on the electricity mix employed. To prevent this indirect environmental implications, in terms of carbon footprint of the EDBM technology due to its relatively high SEC, a straightforward way to circumvent this undesired situation is the use of a low-carbon renewable power source.

In general, the direct integration of desalination with low-carbon renewable energies is mainly accomplished by wind and PV solar power and typically restricted to autonomous small capacity plants [3]. The direct coupling of electrochemical processes and renewable energy for polluted streams [4] or even desalination [5] are well-known approaches in the literature in order to avoid the carbon footprint associated with a large energy consumption. The main advantage of this kind of strategies is that, in terms of primary energy, the SEC per unit of treated volume is almost free of environmental burdens, which makes the process to have a clear eco-innovative behavior. Consequently, the supply of direct current (DC) to electrochemical processes achieved by PV solar energy is described as an interesting alternative (see Table 1) and does not need extra electrical transformations (AC to DC). Other renewable sources such as wind power may have been chosen, but the excellent modularity capacity and potential future developments make PV solar the most desirable option in general.

Published literature regarding PV solar energy combined with electrochemical technologies featured two essential characteristics. The first one is the fact that the DC power supply is typically connected to a regulator system, providing a smooth DC output thanks to batteries. The second feature is that the integrated PV process operates in batch mode or continuous mode but only during short time operations, as shown in Table 1 for the ED technology. This situation of short times strangles the possibility to analyze a critical item such as the solar irradiation profiles, which lead to a variable current intensity for the chosen EDBM process. Therefore, the applied current intensity is time-dependent. Indeed, the stochastic nature of the solar irradiation makes that a proper design and operation is needed to circumvent the application of the time-dependent electricity input rather than a constant (or galvanostatic) one.

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**Table 1**
Selected references of ED and EDBM systems powered by constant and variable current intensity, operating in batch and continuous mode. B stands for batch and Cnt for continuous.

| Power supply | | Constant (grid mix) | | | | Variable (photovoltaic) | | | |
|---|---|---|---|---|---|---|---|---|---|
| Operation mode | | B | Time (min) | Cnt | Time (min) | B | Time (min) | Cnt | Time (min) |
| Technology | ED | [6] | 25 | [7] | – | [8] | 50 | | |
| | | [7] | – | [9] | 1500–3600 | [10] | 90–120 | | |
| | | [9] | 1500–3600 | [11] | – | | | | |
| | | | | [12] | 150 | | | | |
| | EDBM | [13] | 30 | [2] | 420 | | | | |
| | | [14] | 480 | | | | | | |
| | | [15] | 180 | | | | | This work | 1800 |

The prospect of coupling the operation of EDBM in continuous mode instead of batch has been scarcely referenced and no studies were found together with the integration of naturally-variable current input in a whole day. Indeed, the experimental total time of electrochemical processes coupled to PV solar sources tends to be below 500 min. It seems obvious that there is a lack of studies for continuous mode operation, which is the normal mode of operation for large-flowrate facilities as in desalination plants, and even less if coupled to PV solar energy.

For this reason, a novel configuration integrating EDBM with a variable current intensity is depicted in Fig. 1. As it can be seen, there are three material input streams: brine, diluted acid (HCl), and diluted base (NaOH); one energy input as electricity in the form of direct current (constant or variable current intensity); and three output material streams: treated brine, concentrated acid (HCl) and concentrated base (NaOH). As the current intensity is simulating the output of a PV solar array, the benefits in terms of using renewable power sources are clear due to the low-carbon footprint per unit of electrical energy.

The use of a large current intensity can lead to the fact that most of the injected energy is wasted. Even if the generation of acid is assumed to be proportional to the applied current [16], a crossover phenomenon is suggested here to explain the plateau in the acid character versus the applied current [17–19]. Therefore, the additional amount of injected electricity is not transformed into a higher acid/base concentration, leading to higher SEC values.

Taking into account the previous considerations, the aim of this work is the reduction of the SEC of the acid and base production from saline concentrates by means of EDBM under variable current intensity. As a case of study, the production of HCl and NaOH from synthetic seawater desalination brines is selected. The EDBM process operates with a variable current intensity, which simulates the behavior of a real PV solar module under a predetermined solar irradiation profile connected directly to the lab-scale stack. Special emphasis regarding the SEC of the produced acid is provided, considering the fact it is the target product usually reported in the literature. Constant current intensity is studied as reference. The effect of not using the feedback control loop is also included as reference.

## 2. Experimental methodology

### 2.1. Lab scale experimental set-up

All the experiments in this work were performed in a modified PCCell (Germany) bench scale laboratory ED system, composed of different elements as shown in Fig. 2. The main modifications include the peristaltic pumps to work in continuous or semi-continuous mode as well as the SCADA system and measurement equipment. The individual feedback control loops for the pH of the acid and the conductivity in the brine are also inserted in Fig. 2. The controlled variable is the pH of the concentrated acid stream. A set-point is fixed for the pH of the acid. The measured variable is therefore the pH of the acid. The manipulated variable is the flowrate of the diluted HCl stream. Due to the overflow configuration, this flowrate matches exactly the flowrate of the concentrated HCl stream. Disturbances in the pH value are due to the variable current intensity. Zero flowrate of the input diluted HCl will tend to reduce the pH until the maximum value (concentration effect). A relatively large flowrate of the diluted HCl stream will reduce the pH (dilution effect). As later explained, the use of this control loop will help at reducing the SEC. An additional feedback control loop is included regarding the conductivity of the brine tank. For this one, the controlled variable is the conductivity of treated brine stream. A set-point is fixed for the conductivity of the brine. The measured variable is the brine conductivity. The manipulated variable is the flowrate of the input brine stream. The individual components of the lab-scale plant are described next.

#### 2.1.1. Cell stack and membranes

The commercial electrodialysis cell used is composed of two electrodes made of titanium and coated with ruthenium oxide. The effective area of the cathode and the anode is 100 $cm^2$ (square, 10 cm each side). Commercial heterogeneous polyethylene based anion (AM-PP RALEX) and cation (CM-PP RALEX) exchanges membranes were acquired from Mega (Czech Republic). Commercial bipolar membranes (Fumasep FBM) were purchased from Fumatech (Germany). The configuration of the stack is displayed in Fig. 3, following the next sequence CEM/AEM/

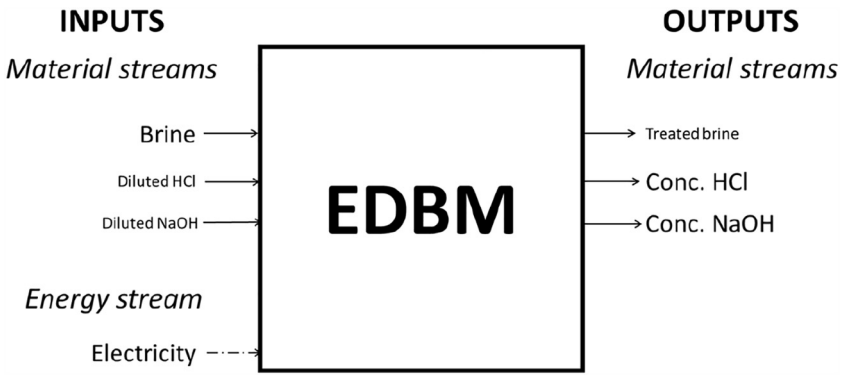


**Fig. 1.** Flowsheet of the EDBM plant.